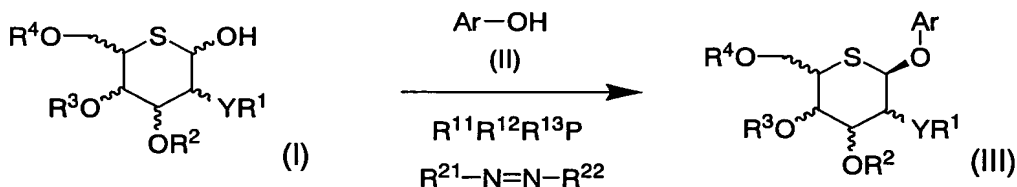


CLAIMS

1. A method for preparing an aryl 5-thio- β -D-
 aldohexopyranoside derivative of Formula (III), which
 5 comprises reacting a 5-thio-D-aldohexopyranose derivative
 of Formula (I) with Ar-OH of Formula (II) in the presence
 of a phosphine represented by $\text{PR}^{11}\text{R}^{12}\text{R}^{13}$ and an azo reagent
 represented by $\text{R}^{21}\text{-N=N-R}^{22}$ in accordance with the following
 scheme:

10



wherein

in the above Formulae (I) and (III),

the wavy lines mean containing any stereoisomer
 15 selected from D-form, L-form and a mixture thereof,

Y represents -O- or -NH-, and

R^1 , R^2 , R^3 and R^4 , which may be the same or different,
 each represent a hydrogen atom, a C_{2-10} acyl group, a C_{1-6}
 alkyl group, a C_{7-10} aralkyl group, a C_{1-6} alkoxy- C_{7-10}
 20 aralkyl group, an allyl group, a tri(C_{1-6} alkyl)silyl group,
 a C_{1-6} alkoxy- C_{1-6} alkyl group or a C_{2-6} alkoxycarbonyl group,
 or

when Y represents -O-, R^1 and R^2 , R^2 and R^3 , or R^3 and
 R^4 may together form $-\text{C}(\text{R}^A)(\text{R}^B)-$ wherein R^A and R^B , which
 25 may be the same or different, each represent a hydrogen

atom, a C₁₋₆ alkyl group or a phenyl group,
in the above Formula (II),

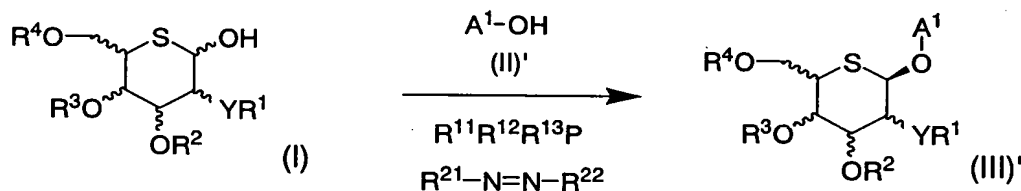
Ar represents an aryl group which may be substituted
with any substituent,

5 in PR¹¹R¹²R¹³,

R¹¹ to R¹³, which may be the same or different, each
represent a phenyl group which may be substituted with a
C₁₋₆ alkyl group, a pyridyl group or a C₁₋₆ alkyl group, and
in R²¹-N=N-R²²,

10 R²¹ and R²², which may be the same or different, each
represent a C₂₋₅ alkoxy carbonyl group, an N,N-di-C₁₋₄
alkylaminocarbonyl group or a piperidinocarbonyl group.

2. The method according to claim 1, wherein



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Formula (II) is represented by the above Formula (II)' and
Formula (III) is represented by the above Formula (III)'
wherein Y, R¹, R², R³ and R⁴ are as defined in claim 1,
wherein in the above Formulae (II)' and (III)',

20 A¹ represents an aryl group which may be substituted
with the same or different 1 to 4 substituents selected
from the group consisting of:

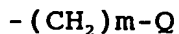
a halogen atom;
a hydroxyl group;

25 -NH₂;

-⁺N(CH₃)₃;

a C₁₋₆ alkyl group which may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom and a hydroxyl group;

5 a group represented by the formula:



wherein m represents an integer of 0 to 4, and Q represents a formyl group, an amino group, a nitro group, a cyano group, a carboxyl group, a sulfonic acid group, a C₁₋₆ alkoxy group which may be substituted with 1 to 4
10 halogen atoms, a C₁₋₆ alkoxy-C₁₋₆ alkoxy group, a C₂₋₁₀ acyloxy group, a C₂₋₁₀ acyl group, a C₂₋₆ alkoxycarbonyl group, a C₁₋₆ alkylthio group, a C₁₋₆ alkylsulfinyl group, a C₁₋₆ alkylsulfonyl group, -NHC(=O)H, a C₂₋₁₀ acylamino group,
15 a C₁₋₆ alkylsulfonylamino group, a C₁₋₆ alkylamino group, an N,N-di(C₁₋₆ alkyl)amino group, a carbamoyl group, an N-(C₁₋₆ alkyl)aminocarbonyl group, or an N,N-di(C₁₋₆ alkyl)aminocarbonyl group;

a C₃₋₇ cycloalkyl group, a C₃₋₇ cycloalkyloxy group,
20 an aryl group, a C₇₋₁₀ aralkyl group, an aryloxy group, a C₇₋₁₀ aralkyloxy group, a C₇₋₁₀ aralkylamino group, a heteroaryl group, or a 4- to 6-membered heterocycloalkyl group, provided that each of these groups may be substituted with 1 to 4 substituents selected from the
25 group consisting of a halogen atom, a hydroxyl group, a C₁₋₆ alkyl group and a C₁₋₆ alkoxy group; and

a group represented by the formula:



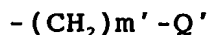
wherein X represents $-(CH_2)_n-$, $-CO(CH_2)_n-$, $-CH(OH)(CH_2)_n-$,
 $-O-(CH_2)_n-$, $-CONH(CH_2)_n-$, $-NHCO(CH_2)_n-$ wherein n represents
an integer of 0 to 3, $-COCH=CH-$, $-S-$ or $-NH-$, and A^2
represents an aryl group, a heteroaryl group or a 4- to
5 6-membered heterocycloalkyl group, each of which may be
substituted with the same or different 1 to 4 substituents
selected from:

a halogen atom;

a hydroxyl group;

10 a C_{1-6} alkyl group which may be substituted with 1 to
4 substituents selected from the group consisting of a
halogen atom and a hydroxyl group;

a group represented by the formula:

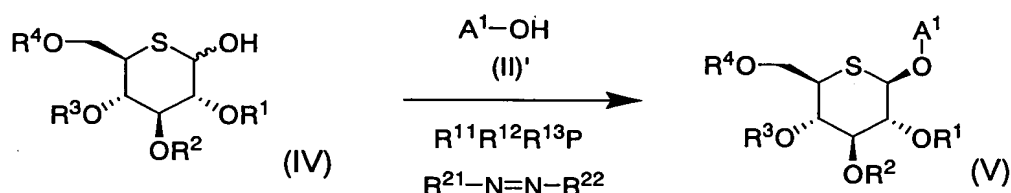


15 wherein m' represents an integer of 0 to 4, and Q'
represents a formyl group, an amino group, a nitro group,
a cyano group, a carboxyl group, a sulfonic acid group, a
 C_{1-6} alkoxy group which may be substituted with 1 to 4
halogen atoms, a C_{1-6} alkoxy- C_{1-6} alkoxy group, a C_{2-10}
20 acyloxy group, a C_{2-10} acyl group, a C_{2-6} alkoxycarbonyl
group, a C_{1-6} alkylthio group, a C_{1-6} alkylsulfinyl group, a
 C_{1-6} alkylsulfonyl group, $-NHC(=O)H$, a C_{2-10} acylamino group,
a C_{1-6} alkylsulfonylamino group, a C_{1-6} alkylamino group, an
N,N-di(C_{1-6} alkyl)amino group, a carbamoyl group, an N-(C_{1-6}
25 alkyl)aminocarbonyl group, or an N,N-di(C_{1-6}
alkyl)aminocarbonyl group; and

a C_{3-7} cycloalkyl group, a C_{3-7} cycloalkyloxy group,
an aryl group, a C_{7-10} aralkyl group, an aryloxy group, a

C₇₋₁₀ aralkyloxy group, a C₇₋₁₀ aralkylamino group, a heteroaryl group, or a 4- to 6-membered heterocycloalkyl group, provided that each of these groups may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom, a hydroxyl group, a C₁₋₆ alkyl group and a C₁₋₆ alkoxy group.

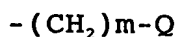
3. The method according to claim 2, wherein



Formula (I) is represented by the above Formula (IV) wherein R¹, R², R³ and R⁴ are as defined in claim 1 and Formula (III)' is represented by the above Formula (V) wherein R¹, R², R³ and R⁴ are as defined in claim 1, and A¹ is as defined in claim 2.

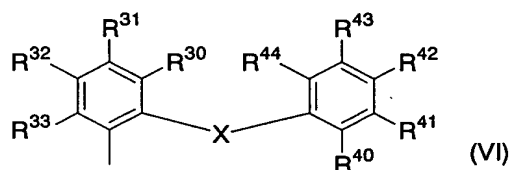
4. The method according to claim 3, wherein A¹ represents a phenyl group substituted with -X-A² wherein X and A² are as defined in claim 2, in which the phenyl group may be further substituted with the same or different 1 to 3 substituents selected from:

- a halogen atom;
- a hydroxyl group;
- a C₁₋₆ alkyl group which may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom and a hydroxyl group;
- a group represented by the formula:



wherein m and Q are as defined in claim 2; and

- a C₃₋₇ cycloalkyl group, a C₃₋₇ cycloalkyloxy group, an aryl group, a C₇₋₁₀ aralkyl group, an aryloxy group, a C₇₋₁₀ aralkyloxy group, a heteroaryl group, or a 4- to 6-membered heterocycloalkyl group, provided that each of these groups may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom, a hydroxyl group, a C₁₋₆ alkyl group and a C₁₋₆ alkoxy group.
5. The method according to claim 3, wherein A¹ is represented by the following formula:



wherein

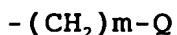
- X represents $-(\text{CH}_2)_n-$, $-\text{CO}(\text{CH}_2)_n-$, $-\text{CH}(\text{OH})(\text{CH}_2)_n-$, $-\text{O}-(\text{CH}_2)_n-$, $-\text{CONH}(\text{CH}_2)_n-$, $-\text{NHCO}(\text{CH}_2)_n-$ wherein n represents an integer of 0 to 3, $-\text{COCH}=\text{CH}-$, $-\text{S}-$ or $-\text{NH}-$,

R³⁰, R³¹, R³² and R³³, which may be the same or different, each represent:

- a hydrogen atom;
- a halogen atom;
- a hydroxyl group;
- $-\text{NH}_3^+$;
- $-\text{N}(\text{CH}_3)_3^+$;
- a C₁₋₆ alkyl group which may be substituted with 1 to

4 substituents selected from the group consisting of a halogen atom and a hydroxyl group;

a group represented by the formula:



5 wherein m represents an integer of 0 to 4, and Q represents a formyl group, an amino group, a nitro group, a cyano group, a carboxyl group, a sulfonic acid group, a C₁₋₆ alkoxy group which may be substituted with 1 to 4 halogen atoms, a C₁₋₆ alkoxy-C₁₋₆ alkoxy group, a C₂₋₁₀ acyloxy group, a C₂₋₁₀ acyl group, a C₂₋₆ alkoxycarbonyl group, a C₁₋₆ alkylthio group, a C₁₋₆ alkylsulfinyl group, a C₁₋₆ alkylsulfonyl group, -NHC(=O)H, a C₂₋₁₀ acylamino group, a C₁₋₆ alkylsulfonylamino group, a C₁₋₆ alkylamino group, an N,N-di(C₁₋₆ alkyl)amino group, a carbamoyl group, an N-(C₁₋₆ alkyl)aminocarbonyl group, or an N,N-di(C₁₋₆ alkyl)aminocarbonyl group; or

a C₃₋₇ cycloalkyl group, a C₃₋₇ cycloalkyloxy group, an aryl group, a C₇₋₁₀ aralkyl group, an aryloxy group, a C₇₋₁₀ aralkyloxy group, a C₇₋₁₀ aralkylamino group, a heteroaryl group, or a 4- to 6-membered heterocycloalkyl group, provided that each of these groups may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom, a hydroxyl group, a C₁₋₆ alkyl group and a C₁₋₆ alkoxy group, and

25 R⁴⁰, R⁴¹, R⁴², R⁴³ and R⁴⁴, which may be the same or different, each represent:

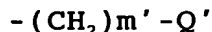
a hydrogen atom;

a halogen atom;

a hydroxyl group;

a C₁₋₆ alkyl group which may be substituted with 1 to 4 substituents selected from the group consisting of a halogen atom and a hydroxyl group;

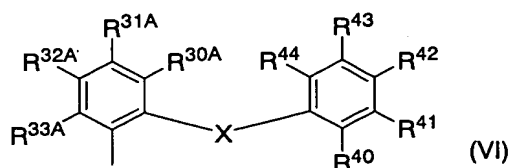
5 a group represented by the formula:



wherein m' represents an integer of 0 to 4, and Q' represents a formyl group, an amino group, a nitro group, a cyano group, a carboxyl group, a sulfonic acid group, a C₁₋₆ alkoxy group which may be substituted with 1 to 4 halogen atoms, a C₁₋₆ alkoxy-C₁₋₆ alkoxy group, a C₂₋₁₀ acyloxy group, a C₂₋₁₀ acyl group, a C₂₋₆ alkoxycarbonyl group, a C₁₋₆ alkylthio group, a C₁₋₆ alkylsulfinyl group, a C₁₋₆ alkylsulfonyl group, -NHC(=O)H, a C₂₋₁₀ acylamino group, 15 a C₁₋₆ alkylsulfonylamino group, a C₁₋₆ alkylamino group, an N,N-di(C₁₋₆ alkyl)amino group, a carbamoyl group, an N-(C₁₋₆ alkyl)aminocarbonyl group, or an N,N-di(C₁₋₆ alkyl)aminocarbonyl group; or

a C₃₋₇ cycloalkyl group, a C₃₋₇ cycloalkyloxy group, 20 an aryl group, a C₇₋₁₀ aralkyl group, an aryloxy group, a C₇₋₁₀ aralkyloxy group, a C₇₋₁₀ aralkylamino group, a heteroaryl group, or a 4- to 6-membered heterocycloalkyl group, provided that each of these groups may be substituted with 1 to 4 substituents selected from the 25 group consisting of a halogen atom, a hydroxyl group, a C₁₋₆ alkyl group and a C₁₋₆ alkoxy group.

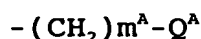
6. The method according to claim 5, wherein A¹ is represented by the following formula:



wherein

X is as defined in claim 5,

- R^{30A} , R^{31A} , R^{32A} and R^{33A} , which may be the same or
 5 different, each represent:
- a hydrogen atom;
 - a halogen atom;
 - a hydroxyl group;
 - a C_{1-6} alkyl group which may be substituted with 1 to
 10 4 substituents selected from the group consisting of a
 halogen atom and a hydroxyl group;
 - a group represented by the formula:

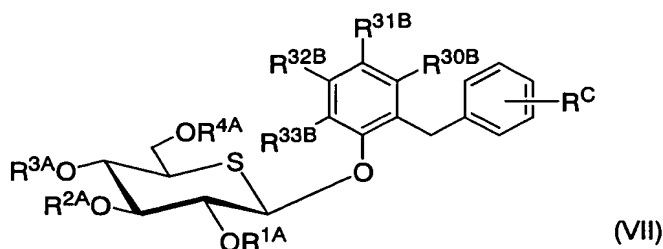


- wherein m^A represents an integer of 0 to 4, and Q^A
 15 represents a formyl group, a carboxyl group, a C_{1-6} alkoxy
 group which may be substituted with 1 to 4 halogen atoms,
 a C_{1-6} alkoxy- C_{1-6} alkoxy group, a C_{2-10} acyloxy group, a C_{2-10}
 acyl group, a C_{2-6} alkoxycarbonyl group, a C_{1-6}
 alkylsulfonyl group, or a C_{2-10} acylamino group; or
 20 a C_{3-7} cycloalkyl group, a C_{3-7} cycloalkyloxy group,
 an aryl group, a C_{7-10} aralkyl group, an aryloxy group, a
 C_{7-10} aralkyloxy group, or a C_{7-10} aralkylamino group,
 provided that each of these groups may be substituted with
 1 to 4 substituents selected from the group consisting of
 25 a halogen atom, a hydroxyl group, a C_{1-6} alkyl group and a

C₁₋₆ alkoxy group, and

$R^{40}, R^{41}, R^{42}, R^{43}$ and R^{44} are as defined in claim 5.

7. The method according to claim 3, wherein the compound of Formula (V) is a compound represented by the following formula:



wherein R^{30B}, R^{31B}, R^{32B} and R^{33B}, which may be the same or different, each represent a hydrogen atom, a halogen atom, a C₁₋₆ alkyl group, a C₁₋₆ alkoxy group, a C₁₋₆ alkoxy-C₁₋₆ alkoxy group, a carboxyl group, a C₂₋₆ alkoxycarbonyl group, a hydroxyl group or a hydroxy-C₁₋₄ alkyl group, R^C represents a hydrogen atom, a halogen atom, a C₁₋₆ alkyl group, a C₁₋₆ alkoxy group, a hydroxy-C₁₋₄ alkyl group, a halogen-substituted C₁₋₆ alkyl group or a C₁₋₆ alkylthio group, R^{4A} represents a hydrogen atom, a C₂₋₆ alkoxycarbonyl group or a C₂₋₆ alkanoyl group, and R^{1A} to R^{3A}, which may be the same or different, each represent a hydrogen atom, a C₂₋₈ alkanoyl group or a benzoyl group.

20 8. The method according to claim 3, wherein the compound of Formula (V) is a compound represented by the following formula:



5

9. The method according to claim 1, wherein Ar is an

10

11. The method according to claim 5, wherein at least one of R^{30} , R^{31} , R^{32} and R^{33} is an electron-withdrawing group.

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13. The method according to claim 7, wherein at least one of R^{30B}, R^{31B}, R^{32B} and R^{33B} is an electron-withdrawing group.

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